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Factors Affecting the Dissolution Rates of Limestones in Acid Media

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DISSERTATION

PRESENTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

BY

HERBERT FRICK KRIEGE

L. C.

The Ohio State University
1926
Published, 1929.

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WITH THE INCREASING USE of limestone in the industries, the factors affecting the rate of dissolution of limestone are assuming practical as well as academic interest. A great mass of literature has appeared on the commercial uses of lime and limestone, but the number of published investigations bearing on the specific differences of limestones and the conditions controlling the rate of dissolution is small. Noteworthy among the contributors to the agricultural phases of the subject are Ames and Schollenberger (1), Barker and Collison (3), White (22), MacIntire and Shaw (15), Hopkins (10), Frear and Thomas (7) and Stewart and Wyatt (20). Their reports of observations of field, small plot and pot tests indicate that fineness is of considerable importance, but their recommendations regarding the degree of fineness desirable in the treatment of acid soils, etc., vary widely. The relative inefficiency of the coarser sizes of limestone particles has been reported, it having been observed that limestone chips lie almost unaltered through long periods in contact with acid soils. Hager and Kern (8) showed that the origin and specific character of limestone may affect its solubility in solutions of carbon dioxide. Morgan and Salter (17) found that the physical properties of limestone, such as hardness, porosity, crystallinity and density were not safe indices of their dissolution rates in acid soils and in acetic acid solutions. The factor most seriously altering the normal solubility of such material was observed to be the magnesium carbonate content; in general the higher the percentage of magnesium carbonate the slower the dissolution.

The factors of greatest importance to the rate of chemical reactions, such as limestone dissolving in an acid solution, are acid intensity, diffusion, surface exposed to reaction and temperature. The other conditions being kept constant, the rate of dissolution of limestone in an acid medium is governed by the amount of surface exposed. If the amount of surface can be determined, it is possible to predict from a dissolution study of this surface the amount of material which would pass into solution under similar conditions from other surfaces of the same composition.

(A) Surface Versus Size of Particles:

The relationship between the surfaces and the dimensions of particles of any *regular* shape is a constant for all sizes of that shape. Hence, it follows that a knowledge of the dimensions of such particles may serve in place of a determination of their surfaces. For an irregularly shaped particle, such as a fragment of limestone as it comes from the crusher, one may doubt that the same irregularities persist in kind and degree as the particle is reduced in size by mechanical means. However, the assumption can be made, for relative purposes, that the factor between the average linear dimension or diameter and the surface of a particle will not change materially as the particle is reduced in size. The validity of this assumption was tested in the following manner, with crystalline material, such as calcite, and with limestone to which no regular crystal habits could be ascribed.

From hand specimens which appeared to be uniform were taken pieces that were large enough to be convenient for grinding and polishing on the lap and oilstones. Regular geometric figures whose surfaces could be accurately measured with a micrometer were worked out. It was attempted to follow as much as possible the most evident cleavage and fracture planes of the limestone chosen since shape would affect the relation between the weight and the exposed surface. Several pieces so fashioned were measured carefully for their total surfaces exposed, weighed and subjected to an acid solution under uni-

form agitation and constant temperature for a definite period. From the loss in weight found, the rate of dissolution per unit of surface could be calculated for each material.

The remaining portion of each original hand specimen was then reduced in a jaw crusher and screened according to the Tyler standard screen scale into the following separates, in meshes per inch—3, 4, 6, 8, 10, 14, 20, 28, 35, 48, 65, 100, 150 and 200. In the following table are given the average diameters of particles of each separate and the increases in surface corresponding to the several screen sizes.

From the values given in Table 1, it will be seen that the average diameter of particles of one separate is 1.414 (square root of 2) times the average diameter of particle of the next finer separate. If the shape of the fragments remains essentially the same, the total surface of a given weight of particles from one separate must be multiplied by this same factor (1.414) to equal the total surface of the same weight of particles from the next lower separate.

TABLE 1—SCREEN MESH IN RELATION TO THE DIAMETERS AND SURFACES OF CORRESPONDING PARTICLES

Mesh of screen	Opening in inches	Average diameter of separates	Increase of unit surface
3	0.263		
		0.224	1.0
4	0.185		
		0.158	1.414
6	0.131		
		0.112	2.00
8	0.093		
		0.079	2.828
10	0.065		
		0.056	4.00
14	0.046		
		0.0394	5.656
20	0.0328		
		0.028	8.00
28	0.0232		
		0.0198	11.312
35	0.0164		
		0.0140	16.00
48	0.0116		
		0.0099	22.624
65	0.0082		
		0.0070	32.00
100	0.0058		
		0.0050	45.248
150	0.0041		
		0.0035	64.00
200	0.0029		

The separates were freed from adhering dust by washing and by shaking with a gentle current of air moving through the screens. Portions of these separates were then taken equalling the weights of the polished pieces of known total surface. Under the same conditions of acidity, temperature and time, the amounts of material dissolved from the several portions were determined. As the only variable remaining was the surface exposed, this became known for the series of separates. While the conditions of the process had to be modified for the kinds of limestone under test, the following are typical for limestones of high calcium content: A weighed sample was placed in a 300-cc. Erlenmeyer flask containing about 250 cc. of a 0.150N HCl solution, which was also 0.2N with respect to calcium acetate for its buffer effect. The acid present was 100-120% in excess of the limestone samples' neutralizing power. The flask was shaken on a mechanical shaker for 4.5 minutes, the suspension being allowed to settle with slow decantation during the next 30 seconds, after which the reaction was quickly stopped by the addition of 150-250 cc. of distilled water at 0 deg. C. Further decantations and washes with cold water followed until the sample could be safely filtered upon a Gooch filter. After drying and reweighing the Gooch crucible, the per cent loss was determined for each separate. During the dissolution process the temperature was kept at 25 deg. C. $\pm$ 0.5 deg.

In the following graph (Chart 1) are shown the curves representing the values of the surfaces derived theoretically by increasing each previous value by the constant factor of 1.414 and those values actually obtained from equal weights of the various screen separates. It is evident that there is no radical departure from the regular relation between the surface and the diameter of a particle of irregular shape, as its size is reduced by crushing. It will be noted that most of the experimental values lie slightly above those calculated. This is what we may expect since the theoretical values of the surfaces are the least which can be obtained under given conditions of progressive decrease in dimension of the particles. The

normal departure from this would mean greater irregularity and hence greater surface exposure.

The curve "DLP" is seen to follow the calculated curve quite closely until the 35- to 48-mesh separate is reached, and here a break occurs followed by a slowly rising trend. It is hardly to be supposed that there is a sudden deviation from the surface increase with decreasing size, particularly not with this specimen, since it is a well crystallized limestone of moderate magnesium carbonate (23%) content. The interpretation lies rather in the fact that the material is not homogeneous, and that selective dissolution is taking place. The break in the surface curve indicates that the readily soluble portion has been dissolved from the exposed surface and that further solution must necessarily be from the more slowly soluble constituent. This matter of selective solubility will be discussed later.

Since this method of studying the surface-size relationship of irregular limestone particles was developed, a similar method has been published by Martin, Bowes and Christelow (16). The surfaces of silica sand separates produced during grinding were determined by the loss in weight in hydrofluoric acid solutions. Very satisfactory results are credited to this procedure.

(B) Effect of Size Upon the Dissolution Rate: Method I.

Having established the persistence of the surface-size relationship of irregularly shaped limestone particles through the sizes from 4- to 150-mesh, it was possible to proceed to the study of the rates of dissolution of limestone particles in acid media. The first apparatus used consisted essentially of a reaction chamber containing an acid solution and the sample, an absorbing electrolyte for the evolved carbon dioxide, a constant temperature bath, and the electrical apparatus needed for making conductivity measurements of the absorbing electrolyte. As the study included 13 screen separates, the apparatus was made in multiple so that seven sizes could be run simultaneously, one separate being run again in the next series to serve as a check test.

The reaction chambers used were gas-scrubbing towers of 275-cc. capacity fitted with ground glass joints. They were charged with 250-cc. of a saturated solution of suc-

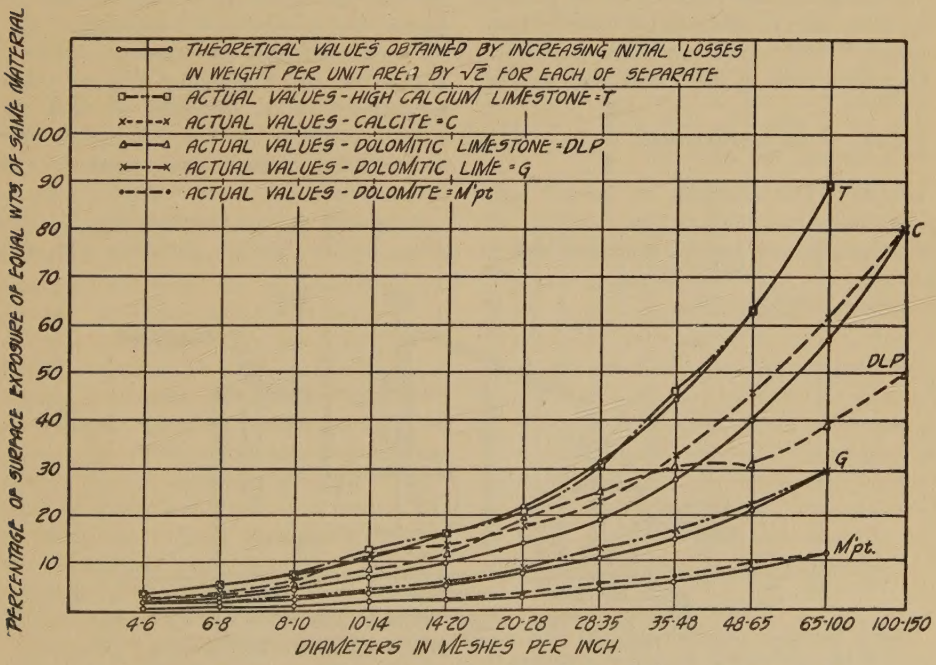

Chart 1. Relation of diameter to total surface of limestone particles

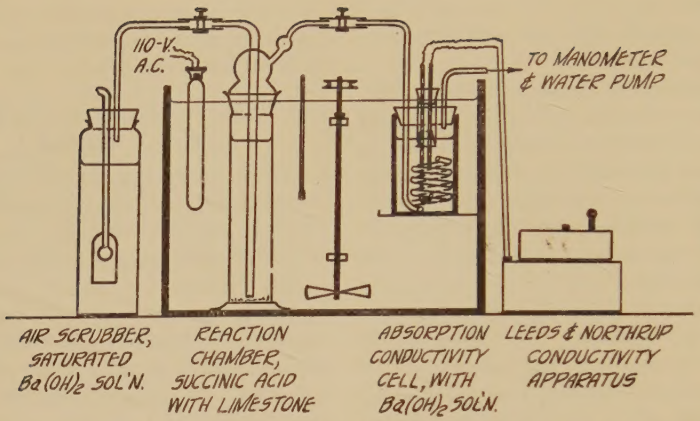
110-V. A.C.
TO MANOMETER & WATER PUMP
AIR SCRUBBER, SATURATED Ba(OH)2 SOL'N.
REACTION CHAMBER, SUCCINIC ACID WITH LIMESTONE
ABSORPTION CONDUCTIVITY CELL, WITH Ba(OH)2 SOL'N.
LEEDS & NORTHRUP CONDUCTIVITY APPARATUS

Fig. 1. Apparatus for dissolution study by the conductivity method

cinic acid ($COOH \cdot CH_2 \cdot CH_2 \cdot COOH$), to which had been added 3 g. of calcium succinate per liter for its buffer effect. This acid was chosen because it provided a solution of moderate acidity (3.24 to 3.27 pH at 25 deg. C.), whose acid intensity could readily be kept constant because of its low solubility (6.8 g. per 100 cc. at 20 deg. C.). One gram portions of the limestone separates were placed in the reaction chambers. The carbon dioxide liberated by the reaction with the succinic acid was led under reduced pressure (0.5 atmosphere) into absorption electrolytic cells of the Vanier type containing 175 cc. of approximately $\frac{N}{8}$ $Ba(OH)_2$ solution. The electrodes of the cell were platinum wires sealed in Pyrex tubing, the exposed platinum tips being melted back in an oxygen-gas flame to form beads slightly over 1 mm. in diameter. The bead-tips were platinized by immersing them in a platinic chloride solution while a direct current of six volts was passed between them, the current being reversed every half minute for four minutes. The original conductivity and concentration of the $Ba(OH)_2$ solution of each cell having been determined, any change produced therein by the absorption of CO_2 and the precipitation of $BaCO_3$ could be traced by conductivity measurements.

For this purpose the apparatus consisted of a Leeds and Northrup Kohlrausch slide wire, a microphone oscillator of 1000 frequencies, a fixed resistance box of 1 to 9999 ohms capacity, head phones, rheostat, 6-volt battery and a 7-way distributor.

As shown in the accompanying diagram (Fig. 1) the reaction chambers and cells

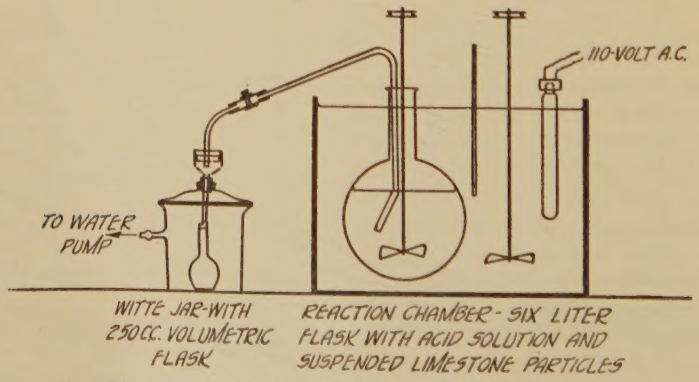
110-VOLT A.C.
TO WATER PUMP
WITTE JAR-WITH 250 CC. VOLUMETRIC FLASK
REACTION CHAMBER - SIX LITER FLASK WITH ACID SOLUTION AND SUSPENDED LIMESTONE PARTICLES

Fig. 2. Dissolution of limestone apparatus

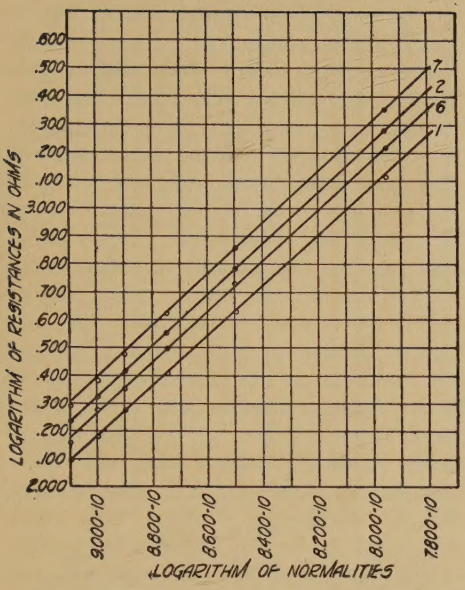

Chart 2. Relation between normality and conductivity of barium hydroxide solutions

were immersed in a thermostat bath, the temperature being maintained at 25.0 deg. C. ± 0.1 deg. The gas train was swept by a current of air purified by a saturated Ba $(OH)_2$ solution. The rate of air passage through the system was 250 cc. per min., this being sufficient to keep the solutions in gentle agitation. Before a run was begun, air was drawn through the apparatus for 30 min. to allow the conductivity cells to reach an equilibrium.

To standardize the cells and to coordinate the resistances found with the amount of limestone dissolved, two methods were employed. The first consisted of placing 1 g. of pure precipitated calcium carbonate in 0.2000 g. portions in the apparatus, the conductivity measurements being made after each addition until the readings became constant. By plotting the observed readings against known weights, intermediate values could be determined. The other method was to dilute the original Ba $(OH)_2$ solution with redistilled water to produce the same decreases in strength which given amounts of pure calcium carbonate yield upon decomposition. As seen in the accompanying graph (Chart 2), plotting the logarithms of the resistances against the logarithms of the normalities of the solutions give parallel straight lines, the initial points depending upon the cells constants.

The mathematical expression for the relationship between the resistances observed and the amounts of limestone decomposed may be had from the slope formula:

$$Y_1 - Y_2 = M\ (X_1 - X_2)$$

From the graph we find that the ordinate-abscissa ratio = 0.9395, which value equals M in the above expression. From this we get:

Log. resistance (R) = cell constant (K) 0.9395 log. normality (N)

and log. R_1 — log. R_2 = 0.9395 (log. N_1 — log. N_2)

$$\text{or log. } \frac{R_1}{R_2} = 0.9395\ \frac{N_1}{N_2}$$

or for convenience

$$1.0644 \text{ log. } \frac{R_1}{R_2} = \text{log. } \frac{N_1}{N_2}$$

In the work of Cain and Maxwell (4) it was found that the best concentration of Ba $(OH)_2$ solution for the complete and rapid absorption of CO_2 in a combustion train was between 0.20 and 0.25 normal. As rapidity of solution was not of prime importance in the present work, a lower strength of Ba $(OH)_2$ was used, namely 0.1210 normal. In 175 cc. of this solution there are 1.8147 g. $Ba(OH)_2$, equivalent to 1.0599 g. of pure $CaCO_3$. The CO_2 from the decomposition of 0.00875 g. of pure $CaCO_3$ produced a

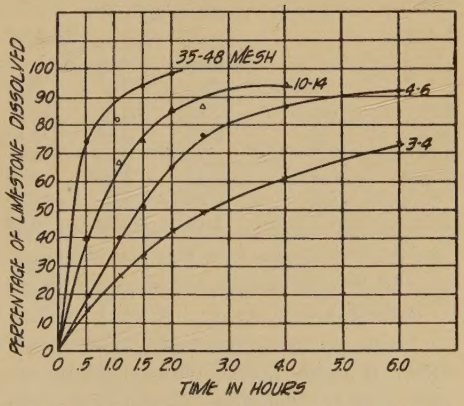

Chart 3. Dissolution rate of high calcium series in saturated succinic acid solution

change of 0.001 in the normality of the absorbing solution. While the actual change in the concentration of the absorbing solution for a given amount of CO_2 is the same at all concentrations, the relative change in the normality is very different, the resistances representing absorptions changing relatively much more as the solution decreases in strength. Therefore, the least sensitivity is found at the beginning of the run while the absorbing solution is almost at its original strength. The same inaccuracy in making the resistance measurement which would involve an error 0.44% $CaCO_3$ at the start would cause a difference of but 0.044% $CaCO_3$ when the determination was nearing completion. As the apparatus was sensitive to differences of this order, its accuracy was considered satisfactory for the present problem.

Three limestone samples were selected for the study of the rate of dissolution under the described conditions. One was a high calcium limestone of the Columbus formation, near Columbus, Ohio, dense, hard, with a splintery fracture. The second was a high magnesium stone approaching the true dolomitic ratio of $CaCO_3$:$MgCO_3$, quite porous and friable, with few visible impurities. This stone was taken from the Niagarian formation, near Carey, Ohio. A large crystal of calcite was the third sample, which was taken as a standard for comparison. Composite samples of the three materials showed the following composition:

TABLE 2—COMPARISON OF CHEMICAL ANALYSES

	High calcium %	High magnesium %	Calcite %
Loss on ignition	39.40	46.51	44.28
Silica	7.07	0.25	0.10
Alumina	1.72	0.15	0.02
Ferric oxide	2.27	0.17	0.20
Calcium oxide	47.45	31.23	54.36
Magnesium oxide	1.19	21.42	0.84

The results obtained in this solution study are shown in the accompanying graphs (Charts 3, 4 and 5).

It will be seen that the type of curves shown is hardly that of normal solution under constant conditions. There is a slight tendency of the curves to flatten out in some cases. This may be accounted for in part by the time which elapsed between the instant of CO_2 formation at the surface of the limestone in the acid medium and the final absorption of the gas in the cell. The effect could not have been great, however, judging from the regularities of the short-time runs. The most pronounced deviations from the expected type of curve must be attributed to the limestones themselves. It was noted that some of the samples disintegrated in the acid medium into many smaller particles instead of dissolving uniformly as unit pieces. Such a process materially affected the dissolution rate through the exposure of a much greater surface area. The larger particles profited more by this than did the smaller sizes, especially if there was a definite size below which the grosser particles did not disintegrate readily. This effect was noted frequently, the dissolution rate of the larger separates being relatively too high from theoretical considerations.

During the early stages of dissolution this effect was not felt, hence the values obtained during this time are found to agree quite closely with the straight line relation between the logarithmic values of both dissolution rate and size of particle. It follows, therefore, that the time of dissolution of

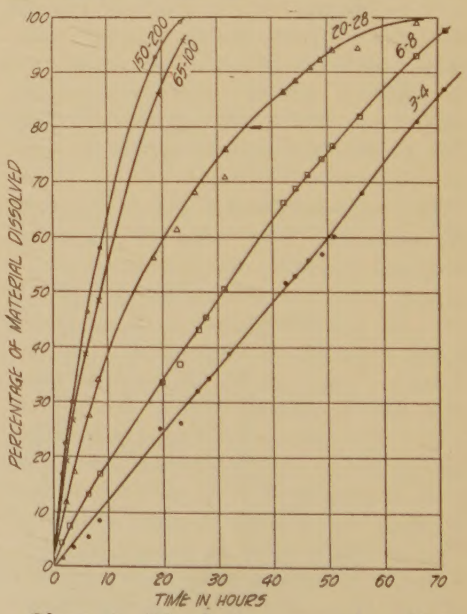

Chart 4. Dissolution rate of a high magnesiub limestone in saturated succinic acid solution

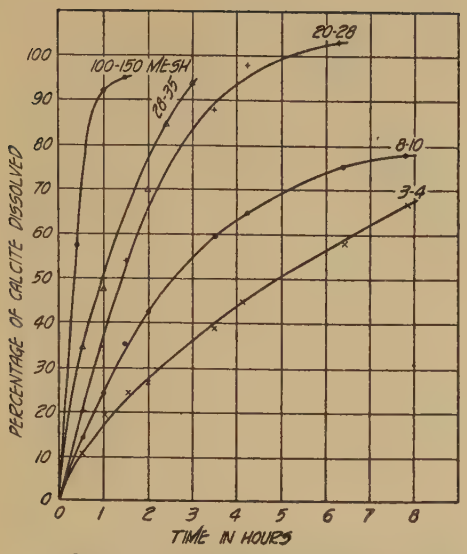

Chart 5. Dissolution rates of the calcite series in saturated succinic acid solution

limestone particles depends upon their diameters. A particle two units in diameter requires twice as much time for its complete dissolution as does a particle of unit diameter under the same conditions.

Method II.

In order to study the rates of dissolution of limestone particles in acid solutions more quickly and with apparatus that can be obtained easily in a general laboratory, the following plan was adopted: A weighed quantity of the screened separate to be studied was placed in a dilute acid solution and kept in agitation until solution was complete. At definite intervals portions of the suspension were withdrawn in such a manner that the remaining liquid and solids were not disturbed in their relative proportions. The withdrawn portions were rapidly filtered and titrated for the acid remaining, the process of neutralization being followed in this manner in successive portions.

The apparatus (Fig. 2) consisted of a 6-liter flask immersed in a constant temperature bath. The flask was equipped with a stirrer driven at 1060 r.p.m., this rate being sufficient to keep the solution and suspended limestone in a quite uniform state of distribution throughout the flask. A measured volume (usually 4.5 liters) of 0.150N. HCl was placed in the flask. The solution contained enough calcium acetate to be 0.20N. with respect to this salt. When the contents of the flask reached the desired temperature of 25 deg. C. ± 0.10 deg., a weighed sample of a limestone separate was admitted to the flask, a decimal stopwatch being started simultaneously. The amount of limestone added was the calculated equivalent of one-half the total acid present. In a Witte jar was placed a 250-cc. volumetric flask having the neck cut off to deliver exactly 250 cc. when filled to capacity. The jar top was fitted with a small Büchner funnel provided with strong rapid filter paper and a large one-hole stopper. The delivery tube connecting this with the solution in the flask was of 6 mm. bore. This tube was adjustable as to the depth of immersion in the reacting solution, being kept at the middle (vertically) of the volume of the liquid. At carefully timed intervals the pressure in the Witte jar was reduced by a water pump and a quantity of liquid and solid material was brought over upon the Büchner funnel. Since this was truly representative of the suspension at the time it could be removed without disturbing the liquid-solid ratio of the remainder. The time of filtration was 15 to 20 seconds. The contents of the 250 cc. flask were transferred to a 500 cc. Erlenmeyer flask, heated to just 95 deg. C. while being stirred with a thermometer, and titrated while hot against standardized 1.000N. sodium hydroxide solution, phenolphthalein being used as the indicator. The amount of acid neutralized in a given time was then calculated to the per cent of limestone dissolved.

The samples used in these tests were hand specimens selected to fairly represent single stratifications of limestone as to uniformity, color and texture. These were then crushed and screened as before and carefully cleaned of adhering dust. After the rate of dissolution determination had been made on a number of separates of each sample selected to give a wide range of sizes, composites of separates were made to determine if the per cent dissolving from such a composite was equal to the sum of those from the component separates. This was found to be the

case. The dissolution curves are shown in the following graphs (Charts 6, 7, 8, 9 and 10). The composites indicated are composed of equal parts of the same material of these sizes—20 to 28, 48 to 65 and 150 to 200-mesh.

The types of curves obtained by plotting the percentages of limestone dissolved against the time of solution are about in accord with the theoretical considerations. Again the relation between the logarithms of the solution rates during early periods and the logarithms of the diameters of the particles involved is found to be linear (Chart 11). From a knowledge of the diameters of limestone particles it is therefore possible to predict the amount of material becoming available during any period from each of the particle sizes. The time required for the complete dissolution of a limestone particle can be predicted from the knowledge of the dissolution rate of any other sized particle of the same material. Similar observations were made by Haslam, Adams and Kean (9) in their recently published work on the rate of dissolution of commercial lines.

One sample marked "Dolomitic LP" (Chart 8) represents the type of limestones in which incongruous dissolution has its most pronounced effect. From the curves giving its dissolution behavior it will be seen that approximately 60% of its weight became available almost as quickly as did the pure calcite particles of the same mesh. During the remainder of its dissolution its curve corresponds closely with that found for dolomites, such as the sample marked "Dolomite SL" (Chart 9). This behavior is explained more fully under the selective solubility tests described later. The 23% $MgCO_3$ contained in this material seems to be held entirely as the double carbonate of calcium and magnesium, the remaining part of the mixture being calcite. Microscopic examination of the residues from the several portions taken indicate this same presence of dolomite and calcite *mixed* since the least dissolved mineral grains were the ones of high refractive index—ranging from 1.675 to 1.68. Many of the crystals retained their sharp outline and unaltered appearance after the greater mass of material had passed into solution.

(C) Composition and Dissolution Rate

The observation that larger particles of dolomitic limestones tended to disintegrate rather than to dissolve as units when in contact with acid media suggested a lack of homogeneity in the material. A *homogeneous* compound or combination of the $CaCO_3$ and $MgCO_3$ in limestones should pass into solution congruently in the presence of an excess of the solvent, provided the solubility of the salts formed would not affect too largely the primary solution reactions. As the matter of congruent or incongruent solution materially affects the dissolution rate of dolomitic limestones from the standpoint of unit particles, the following tests were conducted to determine if selective solubility of the carbonates takes place:

In the first test, three 10-g. portions of a dolomitic limestone of 3 to 4-mesh size were weighed out, the pieces being chosen for apparent uniformity. The samples I, II and III were placed in these respective solutions —250 cc. of 0.205 N. HCl, 500 cc. of 0.1025 N. HCl and 1000 cc. of 0.0501 N. HCl at room temperature and with occasional shaking. After stated intervals these solutions were filtered through Büchner funnels and washed twice by decantation. The residues which were caught on the filter paper were returned to the flasks and other portions of the acid solutions, like the first solvents, were added. The filtrates were evaporated to convenient volume and the calcium and magnesium were determined in the usual manner, observing the precautions of double precipitation of the calcium oxalate, etc. The results are given in Table 3, above.

TABLE 3—DISSOLUTION OF $CaCO_3$ AND OF $MgCO_3$ FROM DOLOMITIC LIMESTONE IN DILUTE HCl

	I $CaCO_3$·$MgCO_3$	II $CaCO_3$·$MgCO_3$	III $CaCO_3$·$MgCO_3$
Solution A (1.5 hr.)	2.289	1.289	2.509
Solution B (1.83 hr.)	1.641	1.265	1.563
Solution C (1.75 hr.)	1.495	1.228	1.253
Solution D (15.5 hr.)	1.297	1.544	1.255
Solution E (192.0 hr.)	0.898	1.330	1.178
Total	1.487	1.349	1.269

In Series I and III selective solution of $CaCO_3$ has occurred, with an enrichment of the residues in $MgCO_3$. In Series II this

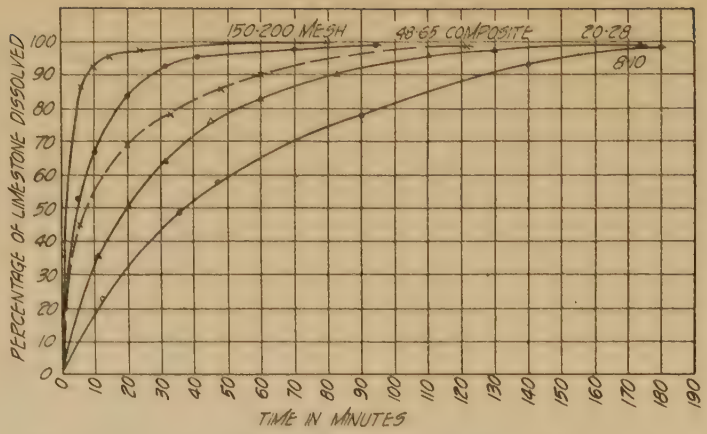

Chart 6. Rate of dissolution of high calcium limestone in dilute buffered solution of hydrochloric acid

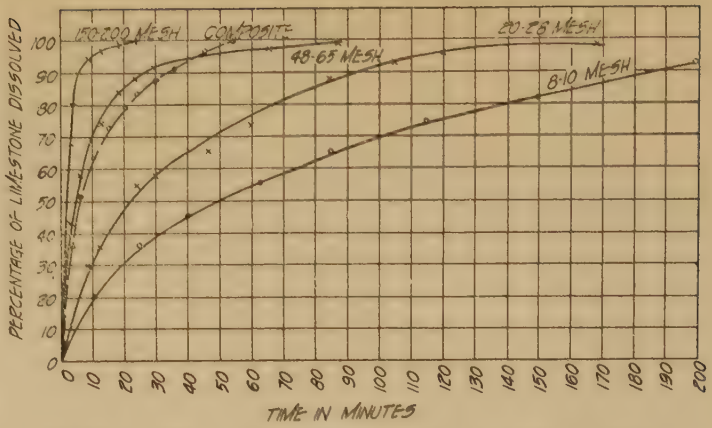

Chart 7. Rate of dissolution of "T" limestone series in dilute buffered solution of hydrochloric acid

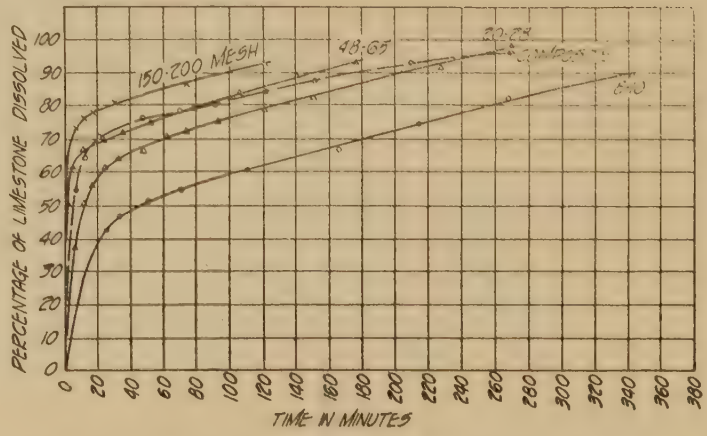

Chart 8. Rate of dissolution of dolomitic "LP" limestone in dilute buffered solution of hydrochloric acid

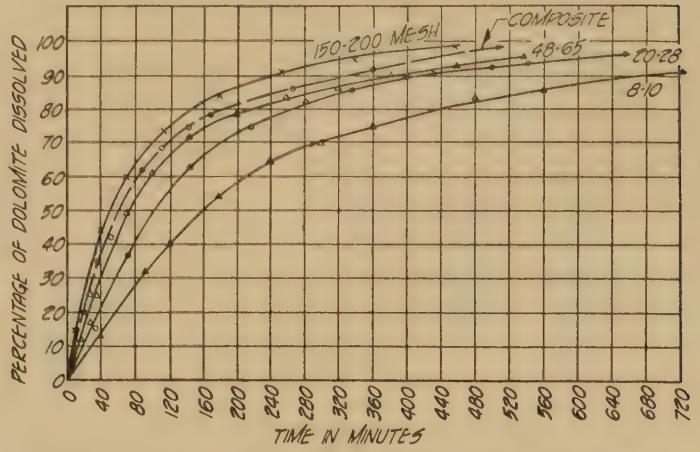

Chart 9. Rate of dissolution of "SL" dolomite series in dilute buffered solution of hydrochloric acid

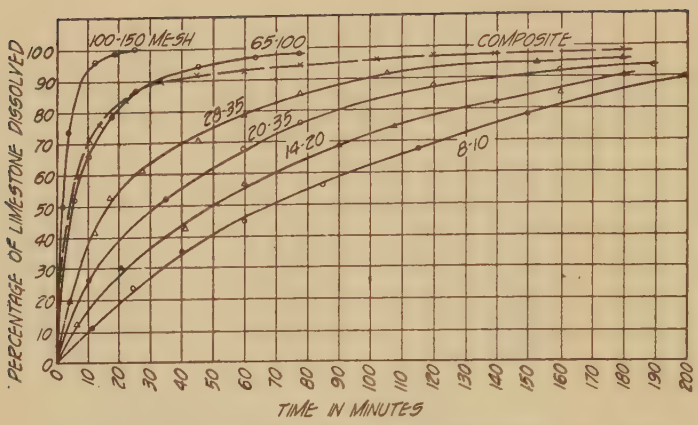

Chart 10. Rate of dissolution of calcite series in dilute buffered solution of hydrochloric acid

tendency is not apparent. It will be noted, however, that the value of the total carbonate ratio decreases with decreasing concentration, as would be expected if a *mixture* of $CaCO_3$ and $MgCO_3$ were in contact with the acid solution.

Using 250 cc. of a saturated solution of succinic acid at 25 deg. C. for 24 hours, the following values were found for the $CaCO_3$: $MgCO_3$ ratios of the material dissolved from 4-mesh particles of a series of dolomitic limestones and dolomites:

TABLE 4—PARTIAL AND COMPLETE DISSOLUTION IN SATURATED SUCCINIC ACID SOLUTION

Limestone used	High magnesium dolomite A	Dolomitic limestone	Dolomite L	Dolomite B
$CaCO_3$:$MgCO_3$ from partial dissolution	1.228	5.797	1.237	1.313
$CaCO_3$:$MgCO_3$ from complete dissolution	1.205	3.479	1.019	1.209

In each case the partial solution contained a higher proportion of calcium to the magnesium present than did the complete solution of these materials.

In order to effect a more complete separation of the fragments falling off a large particle of limestone during dissolution, this plan was followed: Particles of 3- to 4-mesh were suspended in baskets made of glass rods, with sufficient space between the rods to permit particles of 10-mesh or smaller to fall through. The acid solution was contained in a beaker, the lower half of which was filled with a mixture of carbon tetra-chloride and ether having a specific gravity of 1.155. This mixture practically prevented further solvent action on the fallen particles. It was necessary to keep the contents of the beaker gently stirred to overcome the tendency of the dropping fragments to remain at the contact surface between the liquids and thus remain exposed to the acid solution. The average results obtained by this method, using 2 g. of 4-mesh chips of a finely crystalline dolomitic limestone immersed in 200 cc. of 1.10N. HCl for 40 minutes, follow:

TABLE 5—THE SELECTIVE SOLUBILITY OF THE MINERAL CONSTITUENTS OF A DOLOMITIC LIMESTONE, AIDED BY MECHANICAL SEPARATION

	Partial dissolution	Residue	Complete dissolution
$CaCO_3$.....	0.6028 g.	0.0357 g.	0.5612 g.
$MgCO_3$	0.1201 g.	0.0297 g.	0.1609 g.
$CaCO_3$:$MgCO_3$	5.019	1.201	3.479

The change in composition during partial dissolution is here too marked to be overlooked. It is interesting to note how near the theoretical dolomitic ratio ($CaCO_3$:$MgCO_3$) of 1.186 the composition of the residual fragments comes. The index of refraction of this residue was 1.678-1.680, corresponding closely with that of dolomite.

The accompanying results were obtained in another series of determinations, using

only half enough acid for complete dissolution.

TABLE 6—THE SELECTIVE SOLUBILITY OF THE CONSTITUENTS OF MAGNESIUM—CONTAINING LIMESTONES IN SEVERAL ACID SOLUTIONS

Acid used	Dolomitic limestone	"High magnesium" dolomite A	Dolomite L
	$CaCO_3/MgCO_3$		
HCl— .1032 N.....	5.286	1.323	1.134
Acetic— .1030 N.....	46.776	1.110	1.266
Acetic— .2573 N.....	63.894	1.188	1.173
Succinic—.1040 N.....	38.724	1.369	1.219
Succinic—.2618 N.....	41.049	1.176	1.202
Samples true ratio....	3.479	1.205	1.019

It will be noted from the foregoing data that the limestones approaching true dolomites in composition suffer only slight changes in their $CaCO_3$:$MgCO_3$ ratio during partial dissolution. In the case of the moderately dolomitic limestones, however, a marked difference is found in the dissolution rates of their mineral constituents. The greatest difference in the selective solubilities of the carbonates of one dolomitic limestone (original $CaCO_3$:$MgCO_3$ ratio being 3.479) is in 0.2573 N. acetic acid, where the ratio rises to nearly 64.0. In all cases with this stone there is such a marked difference in the rates of dissolution of $CaCO_3$ and of $MgCO_2$ contained therein that classing these carbonates as in a homogeneous combination or in solid solution does not seem in accord with the facts. It would seem more reasonable to consider this limestone a mixture of a calcium carbonate form with another containing both calcium and magnesium carbonates, perhaps as dolomite.

In several of the limestones studied the presence of considerable masses of pyrite could be established microscopically. It was rather surprising to notice that appreciable amounts of iron passed into solution in competition with the alkaline earth carbonates, later to be largely thrown out of the decreasingly acid solution. The deposition occurred largely on the surface of the chips. This indicates that a limestone particle in soils containing much iron in solution could soon be coated with iron hydroxides or basic salts, resulting in its own elimination from further reaction for a while. Also a highly ferruginous limestone might in a short time become useless as a means of correcting the acidity of soils or of other solutions.

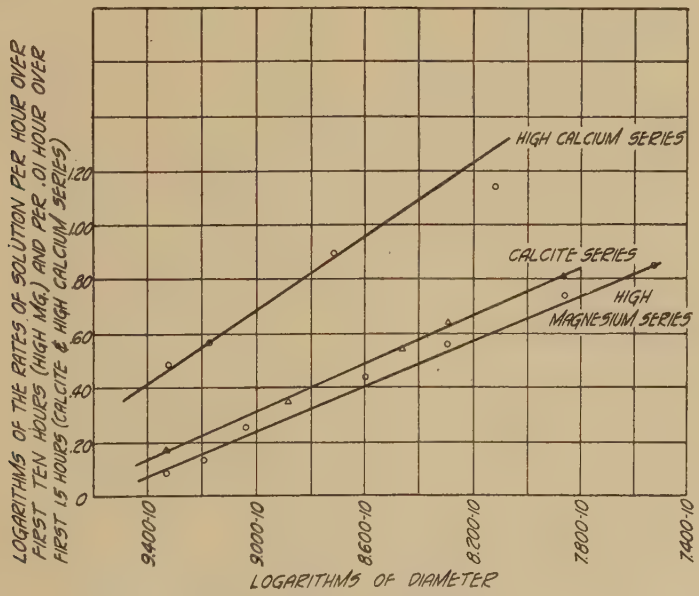

Chart 11. Rate of dissolution of limestone particles in relation to their diameters

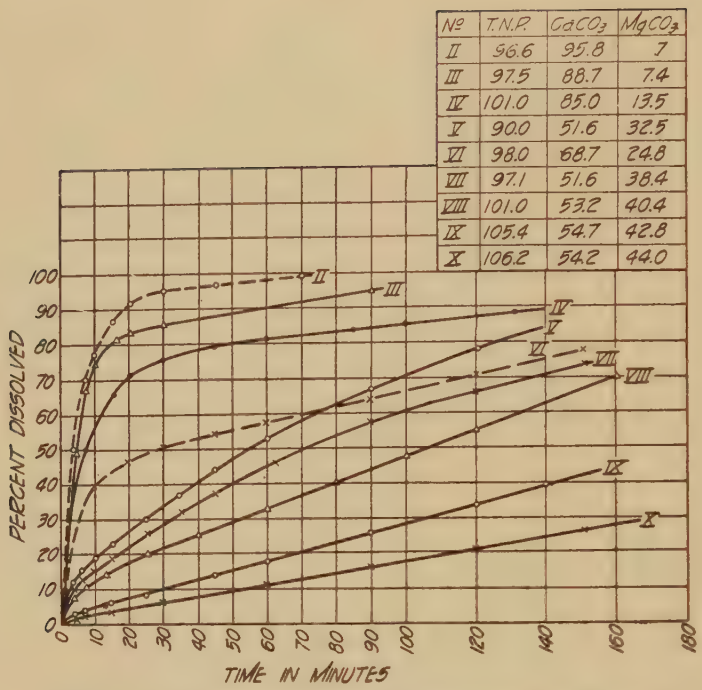

Chart 12. Rate of dissolution of limestones as affected by their composition

In view of the above observed specific differences in limestones with respect to their dissolution tendencies in acid media, any information regarding the state and association of the chief constituents of these materials should be of interest in interpreting results obtained from rate of dissolution studies. The literature describes three definite forms of calcium carbonate, namely, calcite, aragonite, and the hexa-hydrate. Another possible form (gamma- $CaCO_3$) is mentioned, but its instability prevents its occurrence anywhere but under carefully controlled conditions. Aragonite is less stable than calcite, changing into calcite in situ, and hence is less widely found. The solubility of pure aragonite is slightly greater than that of calcite. In the limestones used in these solution studies no aragonite was found using Cole and Little's (6) modified cobalt nitrate solution method.

Of the methods which have been suggested for determining the state of combination of the principal carbonate minerals in limestones, the one developed by Karsten (12) has been most widely adopted. Using dilute acetic acid at temperatures near 0 deg. C. he was able to separate pure dolomite from limestone containing as little as 2% $MgCO_3$ by the more rapid dissolution of the calcitic material. This suggests a mixture of dolomite and calcite in such specimens. Roth (19) and Hunt (11) likewise found the method adaptable to the separation of the calcitic material from the dolomite, as well as dolomitic material from magnesite at higher temperatures. Vesterberg (20) using 1% acetic acid solutions at 0 deg. C. in 25% excess of the equivalent amount for two-hour periods obtained residues closely approaching dolomite from a number of limestones containing magnesium. Retgers and Brauns (18) from similar results state that "there can be no rule of true isomorphism between the double salt $(CaMg).CO_3$ and the component simple carbonates, also not between calcite and magnesite." A number of qualitative tests have been suggested to distinguish the simple from the double carbonates of calcium and magnesium. Perhaps the best is that produced by Lemberg (14) using $AlCl_3$ solution and haematoxylin (log-

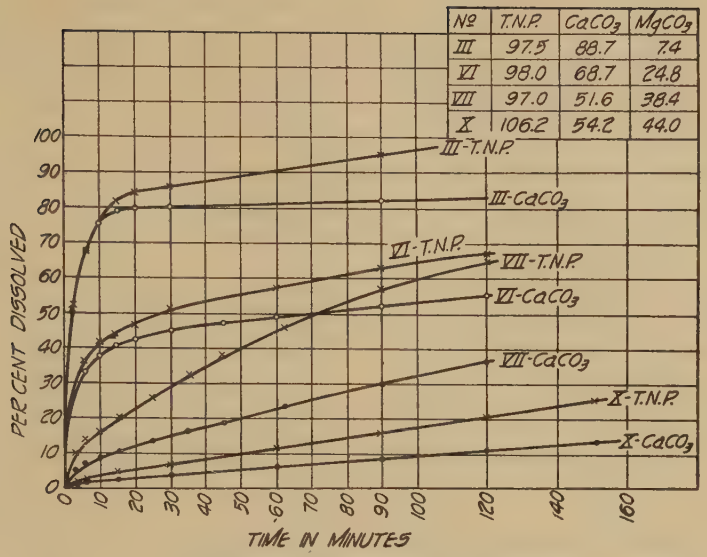

Chart 13. Neutralization of acid by limestones. Total neutralizing power vs. $CaCO_3$ dissolved

wood extract) to produce violet coloration on calcite and none on dolomite or magnesite after boiling for 25 minutes.

As solution behavior is the most important factor in the formation, alteration and degradation of sedimentary rocks, it is well to point out that some confusion exists in the geological literature regarding the true solubility of $CaCO_3$ and of $MgCO_3$ in water. Rate of dissolution seems to have been mistaken for *total solubility.* Let one quotation suffice—Bain (2) writes: "Since $CaCO_3$, $CaSO_4$, Na_2CO_3, and Na_2SO_4 are many times more soluble than $MgCO_3$, they would remain in solution, allowing a relatively pure precipitate of $MgCO_3$ to form." This statement is clearly not in agreement with the known solubilities, since Landholt-Bornstein (13) quote the solubility of pure $CaCO_3$ in CO_2-free water at 25 deg. C. as being $1.433 \times 10^{-3} - 1.445 \times 10^{-3}$, while that of $MgCO_3$ is 9.4×10^{-3}. A study of the many analyses of river, lake and sea waters compiled by Clarke (5) shows a much higher concentration of magnesium as compared with calcium in lake and sea waters than in streams. The explanation apparently lies in the *time* the respective waters have had to act upon the adjacent rock. It must therefore be understood that $MgCO_3$ is *more* soluble, though *more slowly soluble,* in water than is $CaCO_3$, under both natural and carefully controlled laboratory conditions.

Not only the presence of $MgCO_3$ in limestone but also its state of combination and its distribution are factors of great signifi-

TABLE 7—THE SOLUBILITY OF A DOLOMITIC LIMESTONE IN 1% ACETIC ACID SOLUTION AT 0 DEG. TO 3 DEG. C.

	2.25 hours		4 hours		6.5 hours	
Per cent of residue =	58.80%	59.04%	59.15%	57.67%	58.67%	58.75%
Per cent of $CaCO_3$ in solution =	41.28%	40.46%	41.12%	42.36%	41.01%	41.11%

cance to the rate of dissolution of a specific dolomitic limestone. Thus with a limestone containing 22% to 23% $MgCO_3$ a high rate of dissolution was observed during the early part of its decomposition, with a decided decrease in the rate during the later stages of the process. The reason for this break in the dissolution curve is found in the results of the following procedure.

Duplicate weighed samples of 150- to 200-mesh material were treated with 25% excess of 1% acetic acid solution at 0 deg. to 3 deg.

C. for stated periods. The undissolved residues were collected by rapid filtration on weighed Gooch crucibles, washed, dried and weighed. The filtrates were analyzed in the usual manner for calcium, with the results shown in Table 7.

This indicates that the dissolution of the more quickly soluble calcite in this sample is as complete in 2¼ hours as in 6½ hours, and that a very slowly soluble portion is left. Since the original material contained 22% to 23% $MgCO_3$, which content was practically untouched during dissolution, the residue had a composition quite closely agreeing with that of Roth's (19) $(3Ca \cdot 2Mg)5CO_3$ "dolomite." Whether or not this is its true state of combination, the above residue, enriched in magnesium during dissolution, represents a definite portion of this limestone which successfully prevented complete and congruous dissolution of the entire stone under these conditions.

The same test was applied to other samples of limestones used earlier in this study. The time allowed for the reaction was in all cases 4½ hours, the other conditions remaining as in the previous test. As the agreement between duplicate samples was close, only the averages are given here:

TABLE 8—SOLUBILITY OF LIMESTONES IN 1% ACETIC ACID SOLUTION AT 0 DEG. TO 3 DEG. C. FOR 4.5 HOURS

	Calcite	Dolomite	Dolomite (SL)	Dolomite (SD)	Dolomite (SB)
Per cent residue =	33.66%	93.97%	90.25%	91.01%	88.72%
$CaCO_3/MgCO_3$ ratio in solution =	No Mg found	3.374	1.313	1.319	1.497

As the dissolution of the calcite was not complete in the time allowed, all of the residual values are somewhat too high. However, the indications are definite enough to characterize the samples. In each case the $CaCO_3$:$MgCO_3$ ratio in solution is higher than that of the original material. The per cent of residue is indicative of the proportion of each stone in which the calcium is held in a very slowly soluble form under the conditions maintained.

Agricultural Application

Agricultural liming materials have been evaulated on the basis of their total neutralizing power and their fineness. It has been shown in this paper what effect fineness has upon the value of limestone judged by its rate of dissolution. It now appears that chemical and mineral composition must be considered.

In order to determine more definitely what effect the chemical composition has upon the dissolution behavior of limestones and dolomites, samples were taken from twenty sources of agricultural liming materials used in Ohio and adjoining states. These were selected to give as wide a range in chemical composition as possible. The samples were carefully screened, the 48- to 65-mesh being chosen for this dissolution work. The test procedure followed was the same as previously described under Method II. The results, with the nine samples covering the composition range, are given in the two preceding charts (Charts 12 and 13).

Several facts are apparent in the foregoing charts: *First,* the rate of dissolution of a stone consisting chiefly of calcium carbonate is much higher than is that of a dolomite. *Second,* the dissolution curve of most of the dolomitic limestones consists of two distinct phases—(*a*) a steeply rising straight line produced almost entirely by the calcium carbonate dissolved; (*b*) a much flatter straight line produced by the dissolution of dolomite. This indicates the existence of these two constituents as a mixture and not in combination. For the moderately dolomitic stones as Nos. IV and VI (Chart 12) the breaks in the curves occur at approximately 70% and 40% respectively. No. X, a dolomite, has no break because it has no appreciable free calcitic material. *Third,* stones of approximately the same composition need not have similar dissolution curves. This is true for both high calcium and high magnesium stones. Since this characteristic governs the effect which can be produced in an acid soil, it is evident that the specific dissolving rate of any limestone *must be determined,* if its effect is to be

compared with that of another stone. *Fourth,* the neutralizing effect of the moderately dolomitic limestones (10% to 30% $MgCO_3$), may be greater in a given time through their uncombined calcium carbonate alone, than that of a practically pure dolomite of higher total neutralizing power.

Conclusions and Summary

The rate of dissolution of a particle depends upon its surface area. In regularly shaped particles the total surface exposure of a given weight of material is inversely proportional to the diameters or linear dimensions of the particles. Hence, dividing the diameter of a particle by two, doubles the surface area of the mass and doubles its rate of dissolution.

Since any limestone has characteristic fracture and cleavage habits, it may be assumed that these habits will persist through all sizes to which the limestone may be reduced by crushing in practice. Under these conditions, the shapes of the particles during crushing will be generally similar. Therefore, a definite relation should exist between the surfaces and the diameters of irregularly shaped particles of this material.

It was found in this investigation that the relation between the decrease in size and the increase in surface of irregularly shaped particles of limestone upon crushing, is a constant one.

It was found, further, that the rate of dissolution of limestone particles in dilute acid media, is inversely related to the particle size.

The rate of dissolution of a limestone in acid media is specific for that limestone and must be determined as such.

The physical properties, such as crystallinity and hardness, do not indicate the specific dissolution rate of a limestone.

Calcite dissolves more rapidly in dilute acids than does dolomite.

The rate of dissolution of limestone is affected greatly by its composition, especially by its content of magnesium carbonate. In general, the higher this content, the lower the dissolution rate, but not in direct proportion to the $MgCO_3$ content.

Certain exceptions to this general statement were found. Some dolomitic limestones containing 15% to 25% $MgCO_3$ were found to dissolve more rapidly during the first half of their dissolution periods than did practically pure calcite and other limestones of high calcium content.

In this investigation the dolomitic limestones observed were shown to be mixtures of the double carbonate of lime and magnesia ($CaCO_3 \cdot MgCO_3$) and $CaCO_3$, with one possible exception, in which the carbonates appeared to be combined as $3CaCO_3 \cdot 2MgCO_3$.

As the dissolution of the more quickly soluble $CaCO_3$ takes place, the residue becomes enriched in its $MgCO_3$ content.

The dolomitic limestones were observed to disintegrate in dilute acids into smaller particles, thus offering new surfaces to the media. As a result, the rate of dissolution of the larger particles of such limestones was somewhat greater than was to be expected from their size.

Under the microscope, the residues from the partial dissolution of dolomitic limestones were found to consist largely of well defined crystals, showing little dissolution effects. The index of refraction of these almost unaltered crystals was found to be 1.68, corresponding to dolomite. This agrees with their chemical composition.

The rate at which limestone dissolves is an important characteristic and should be considered along with its total neutralizing power and the fineness to which it has been crushed.

It is believed that the observations made in these laboratory investigations can be applied in general to field conditions.

The apparatus and test procedures for each of the following determinations have been described—(*a*) the relation between size and surface of irregular particles; (*b*) the effect of size upon the dissolution rate of limestone particles; (*c*) the effect of chemical and mineralogical composition on the dissolution rate of limestones and dolomites; (*d*) selective solubility studies.

* * *

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I, Herbert Frick Kriege, was born in Omaha, Nebr., March 14, 1895. I received my secondary education in the public and high schools of Warrenton, Mo., and in Central Wesleyan Academy. From 1912 to 1916 I was a student at Central Wesleyan College, receiving the degree of Bachelor of Science from that college in 1916. The following three years were spent teaching in the high schools of Clear Lake and Perry, Iowa. During the summer of 1918 work in chemistry was taken at the University of Illinois. From August, 1918, to January, 1919, I was in the Signal Service, Coast Artillery Corps. In September, 1919, I began graduate work in chemistry at the University of Missouri, having been elected to a University Scholarship that year. In 1920 I completed the requirements for the degree of Master of Arts, receiving the degree from this institution the following June. From 1920 to 1923 I served as Instructor in chemistry at the University of Missouri. During the next eighteen months I was employed as chemist by the Missouri State Highway Commission. Since September, 1924, I have been in residence at the Ohio State University as Research Fellow of the National Agstone Association, devoting full time to graduate studies and research leading to the degree of Doctor of Philosophy.

Columbus, Ohio, June, 1926.